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The Photochemistry of Hexachlororhodate(III)

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In recent years, study of the ligand field (L.F.) photochemistry of d^6 metal ion complexes has broadened to include investigations of Rh(III)[1-3] and Ir(III)[4,5] systems. In contrast to the photoinertness characteristic of most Co(III) complexes,[6] these heavier transition metal (T.M.) compounds display substantial photolability upon excitation into the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption band. Photosubstitution quantum yields are typically in the range 0.1–0.9 and sensitization studies[1,2] have clearly demonstrated the excited triplet level ($^3T_{1g}$) as a photoreactive state. Three alternative explanations have been offered to account for the unusual position of Co(III) amongst its d^6 neighbors, all suggestions involving consideration of L.F. strengths. It has been argued[6,7] that for compounds with lower L.F. strength, the small $^1A_{1g} \rightarrow {}^1T_{1g}$ energy gap results in highly efficient $^1T_{1g} \rightarrow {}^1A_{1g}$ internal conversion relative to intersystem crossing to the reactive triplet level $^1T_{1g} \rightarrow {}^3T_{1g}$). The possibility of a substitution-inert quintet level ($^5T_{2g}$) intervening in the relaxation of Co(III) excited states has been discussed;[8,9] and finally it has been suggested that the $^3T_{1g}$ level may lie at an energy below the activation energy for thermal substitution which would imply that it could not react.[10]

Consistent with these models requiring a strong L.F. it is observed that the complexes $Co(CN)_6^{3-}$ and $Co(CN)_5X^{2-}$ are photoreactive[11,12] *i.e.*, Co(III) compounds are labilized by coordination of groups with high L.F. strength. Conversely, we may adduce from the foregoing observations, the prediction that sufficiently low field Rh(III) (or Ir(III)) complexes should exhibit reduced quantum yields. We present here the results of an experimental test of this latter prediction, using the compound $RhCl_6^{3-}$ as a model for a low field Rh(III) system.

The first spin-allowed L.F. transition of $RhCl_6^{3-}$ occurs at 518 nm, which approximates closely that observed for $Co(NH_3)_5Cl^{2+}$. The Rh(III) complex must be studied at low temperature and in intense light because of its thermal lability ($t_{1/2}$ for Cl^- aquation *ca.* 6 minutes at 25 °C).[13] We have irradiated the complex in 0.10*M* $HClO_4$ at 1 °C, using the 700 mW line at 514.5 nm of a Coherent Radiation argon ion laser. The laser beam was first passed through a diffusing lens to minimize possible thermal effects along the solution light path. Irradiations of the order of five minutes produced as much as 30% conversion to $RhCl_5OH_2^{2-}$. Substitution was followed from spectral change at 525 nm employing a Gilford 240 spectrophotometer.[14] After correction for thermal background obtained in parallel runs and actinometry with ferrioxalate[15] we obtain a quantum yield of 0.02_4. This value is at least an order of magnitude below the yields reported by Kelly and Endicott for $Rh(NH_3)_5X^{2+}$ systems. It would appear that as a broad generalization, the requirement for a strong L.F. holds some merit. However, when ligand field strengths do not differ markedly (such as in the $Rh(NH_3)_5X^{2+}$ or $Co(CN)_5X^{3-}$ series) no clear correlation exists between the energy of the long wavelength L.F. band and the degree of labilization.[16,17] Furthermore, it is noteworthy that the photoreactivity of $RhCl_6^{3-}$ is still considerably greater than that recently reported for $Co(NH_3)_5Cl^{2+}$ on $^1A_{1g} \rightarrow {}^1T_{1g}$ excitation (488 nm, $\phi_{NH_3} = 0.005$; $\phi_{Cl} = 0.002$).[6] We cannot at this juncture distinguish between the quintet hypothesis and Endicott's proposed correlation with thermal substitution activation energy.

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